

# Monocrystalline Diamond Paste-Based Electrodes and Their Applications for the Determination of Fe(II) in Vitamins

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**A new class of electrochemical sensors, namely, electrodes based on diamond paste, was designed using monocrystalline diamond (natural diamond 1  $\mu\text{m}$  and synthetic diamond, 50  $\mu\text{m}$  (synthetic-1) and 1  $\mu\text{m}$  (synthetic-2)) powder and paraffin oil. The characterization of the electrodes was performed using cyclic voltammetry and differential pulse voltammetry. Fe(II) was determined by differential pulse voltammetry (DPV) at 75 mV (vs Ag/AgCl) using all diamond paste-based electrodes. The linear concentration range was between  $10^{-8}$  and  $10^{-4}$  mol/L for both the natural diamond and synthetic-2 with detection limits of  $10^{-10}$  and  $10^{-9}$  mol/L, respectively, whereas the linear concentration range for synthetic-1 was between  $10^{-7}$  and  $10^{-3}$  mol/L with a detection limit of  $10^{-8}$  mol/L. Fe(II) was determined successfully from four types of pharmaceutical products. The recovery values of Fe(II) in the pharmaceutical products were higher than 98.00% with relative standard deviation values <5%.**

Explanations regarding the electrical properties (especially conductivity) of diamond were given on several occasions by physicists<sup>1,2</sup> and are based on the mobilities of electrons and holes and on the inherent structural defects of diamond crystals as well as on the presence of small amounts of impurities in its structure. Furthermore, the advances in single-crystal diamond have enabled the development of a wide range of monocrystalline diamond products to meet the exacting requirements of many different applications.<sup>1</sup> Room temperature drift mobilities of 4500 cm<sup>2</sup>/Vs for electrons and 3800 cm<sup>2</sup>/Vs for holes have been measured in high purity single-crystal diamond.<sup>2</sup> These values were determined by using the time-of-flight technique on thick, intrinsic free-standing diamond plates and were verified by current–voltage measurements on p–i junction diodes.<sup>2</sup> The reliability obtained for the electrical properties of single-crystal diamond is encouraging for research in the electrochemical sensors based on monocrystalline diamond. Furthermore, it proves that the doping of this type of diamond is not necessary. That minimizes the time

affected for electrodes' construction and also simplifies the steps adopted for the design of such electrodes.

The literature survey shows that up to now, polycrystalline diamond thin film electrodes have been used increasingly in electrochemical studies because of the low background current, wide potential range, lack of adsorption, and high overpotential for oxygen evolution by water oxidation in aqueous electrolyte solution.<sup>3–13</sup> Boron-doped diamond thin-film electrodes were also used because of their physical and electronic properties, such as hardness, chemical inertness, optical transparency, and high thermal and electrical conductivity.<sup>14,15</sup>

Iron(II) is necessary for hemoglobin production, and iron deficiency results in small red blood cells with insufficient hemoglobin (microcytic hypochromic anemia). Iron(II) is essential to periods of human growth, so its quantitative determination has biological interest. The administration of iron preparations is needed in iron deficiency, which may be due to chronic blood loss, pregnancy (the fetus takes iron from the mother), various abnormalities of the gut (iron absorption may be reduced), or premature birth (such babies are born with very low iron stores). Iron must be in the ferrous form for absorption, which occurs by active transport. In plasma, iron is transported bound to transferrin, a  $\beta$ -globulin.<sup>16</sup>

Up to now, different electrodes were proposed for the assay of Fe(II) in environmental or clinical matrixes, using direct analysis<sup>17–19</sup> and indirect analysis (titration).<sup>20,21</sup> The electrodes

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proposed for the assay of Fe(II) were also used as detectors in flow injection analysis systems<sup>22</sup> and in chromatography.<sup>23</sup>

In this paper, a new class of diamond electrodes is described. A diamond paste similar to carbon paste was preferred for the electrodes' design, since the carbon paste-based electrodes proved highly reliable construction and response characteristics.<sup>24</sup> Three types of diamonds were used for the design of the diamond paste: a natural diamond and two types of synthetic diamond. DPV was used for the calibration of the electrodes as well as for the uniformity content test of Fe(II) in four types of vitamins. The proposed diamond paste-based electrodes have lower limits of detection and higher selectivity over  $\text{Mg}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  if one compares them with the electrodes used until now for the assay of Fe(II).<sup>17–23</sup>

## EXPERIMENTAL SECTION

**Diamond Paste Electrode Design.** All diamond paste electrodes were prepared by mixing 0.1 g of each diamond powder with 20  $\mu\text{L}$  of paraffin oil. A portion of the paste was then placed in a plastic pipet tip (3 mm). The diameter of the sensing part was 2.3 mm. Electric contact was made by inserting a silver wire (0.5 mm in diameter) in the diamond paste. Before each use, the electrode surface was smoothed by polishing with an alumina paper (polishing strips 30144-001, Orion). When not in use, the diamond paste electrode was stored at room temperature.

**Apparatus.** A663VA Stand (Metrohm, Herisau, Switzerland) in combination with a PGSTAT 20 and software (Ecochemie version 4.8) were used for all measurements. A Pt electrode and an Ag/AgCl electrode served as the counter and reference electrodes in the cell.

**Reagent and Materials.** All chemicals were analytical grade. All solutions were prepared by using deionized water. Phosphate buffers (pH 1–10) were prepared by mixing 0.67 mol/L  $\text{KH}_2\text{PO}_4$  (Saarchem-Holpro Analytic) solution with 0.67 mol/L  $\text{Na}_2\text{HPO}_4$  (Chemical Suppliers) solution in different ratios. All solutions of Fe(II) were freshly prepared every day by dissolving the required amount of ammonium ferrous sulfate in deionized water. Monocrystalline natural 1  $\mu\text{m}$  (99.9%) and synthetic diamond 50  $\mu\text{m}$  (synthetic-1) (99.9%) and 1  $\mu\text{m}$  (synthetic-2) (99.9%) powders were purchased from Aldrich (Milwaukee, WI); the paraffin oil was purchased from Fluka (Buchs, Switzerland). Vitaforce 21-PlusBPR Protectavite was supplied by Pharma Natura (Pty) Ltd., Sandton, South Africa. Vital Multi-Vitamin & Mineral with Iron was supplied by Vital Health Foods (Pty) Ltd., Kuils River, South Africa. Weigh-Less daily multivitamin with antioxidants was supplied by Weigh-Less S.A. (Pty) Ltd., Hout Bay, South Africa. Bettaway Iron Extra was supplied by Better Nutrition (Pty) Ltd., Sandton, South Africa.

**Recommended Procedures. Cyclic Voltammetry.** For the optimization procedure, cyclic voltammetry scans were performed using the new diamond paste-based electrodes as working electrodes together with a reference electrode (Ag/AgCl) and an

auxiliary platinum electrode between  $-1.0$  and  $+1.0$  V. The voltammetric scan rate was adjusted to 10 mV/s. All solutions were deoxygenated prior to use by degassing with  $\text{N}_2$ .

**Direct DPV Assay.** The technique used for the direct voltammetric assay was differential pulse voltammetry between  $-25$  and  $+200$  mV, with an applied potential pulse amplitude of 25 mV, scan rate of 10 mV/s, pulse width of 50 ms, and pulse time of 40 ms. All measurements were performed at 25 °C. The diamond paste electrode, together with the reference and auxiliary electrodes, was dipped into a cell containing phosphate buffer (pH 9.0) and sodium pyrophosphate as supporting electrolyte in a ratio of 3.5:1. All solutions were deoxygenated before the measurements with  $\text{N}_2$ . The peak height measured at 75 mV was plotted versus the concentration of Fe(II). The unknown concentrations of Fe(II) were determined from the calibration graphs.

**Content Uniformity Assay of Four Vitamin Tablets.** Ten tablets from Iron Extra (sample 1) and 10 tablets from Vital Multi-Vitamin & Mineral with Iron (sample 2) were individually placed in 10 100-mL calibrated flasks and dissolved in deionized water. Ten tablets from Weigh-Less Daily Multi-Vitamin with Antioxidants (sample 3) and 10 tablets from Vitaforce 21-PlusBPR Protectavite (sample 4) were individually placed in 10 50-mL calibrated flasks and dissolved in distilled water. The direct DPV method was used for the assay of Fe(II) content in each of the vitamin solutions.

## RESULTS AND DISCUSSION

**Optimization of Working Conditions.** To optimize the working conditions, cyclic voltammograms for different electrolyte solutions and pHs (phosphate buffer with the pH between 1 and 10) were recorded before and after adding different aliquots of Fe(II) solution. Five different supporting electrolytes (0.05 mol/L KCl, 0.1 mol/L  $\text{KNO}_3$ , 0.1 mol/L  $\text{NaNO}_3$ , 0.1 mol/L NaCl, and 0.1 mol/L  $\text{Na}_4\text{P}_2\text{O}_7$ ) were tested. Figure 1A–C shows the effect of pH and supporting electrolyte on the peak height. The peaks measured at pH 9.0 (phosphate buffer) in a 0.1 mol/L of  $\text{Na}_4\text{P}_2\text{O}_7$  were higher than the peaks recorded for the rest of the electrolytes at different pHs, with the exception of the ones obtained using the electrode based on synthetic-2. The shape of the peaks also contributes to the selection of the optimum electrolyte and pH. The best peak shape for the three electrodes was recorded at pH 9.0 in the presence of  $\text{Na}_4\text{P}_2\text{O}_7$  solution. Despite the superiority of the peaks obtained when using  $\text{KNO}_3$  as electrolyte, at pH 7.0 (phosphate buffer) for synthetic-1- and synthetic-2-based electrodes, the peaks recorded were broad, resulting in a weak resolution that enhances the influence of interferences in the determination of Fe(II) from real samples. Therefore, the optimum working pH was established to be 9.0 (phosphate buffer), in 0.1 mol/L  $\text{Na}_4\text{P}_2\text{O}_7$  supporting electrolyte.

**Response of the Diamond Paste Electrodes.** The reason for the selection of natural and synthetic diamonds for the electrodes' design is to determine if they behave the same or differently as electrode materials; the comparison between the designed electrodes was possible by selecting the same particle size (1  $\mu\text{m}$ ) for both types of diamonds. The influence of the particle size on the response characteristics of the electrodes was determined by the utilization of a synthetic diamond with a larger

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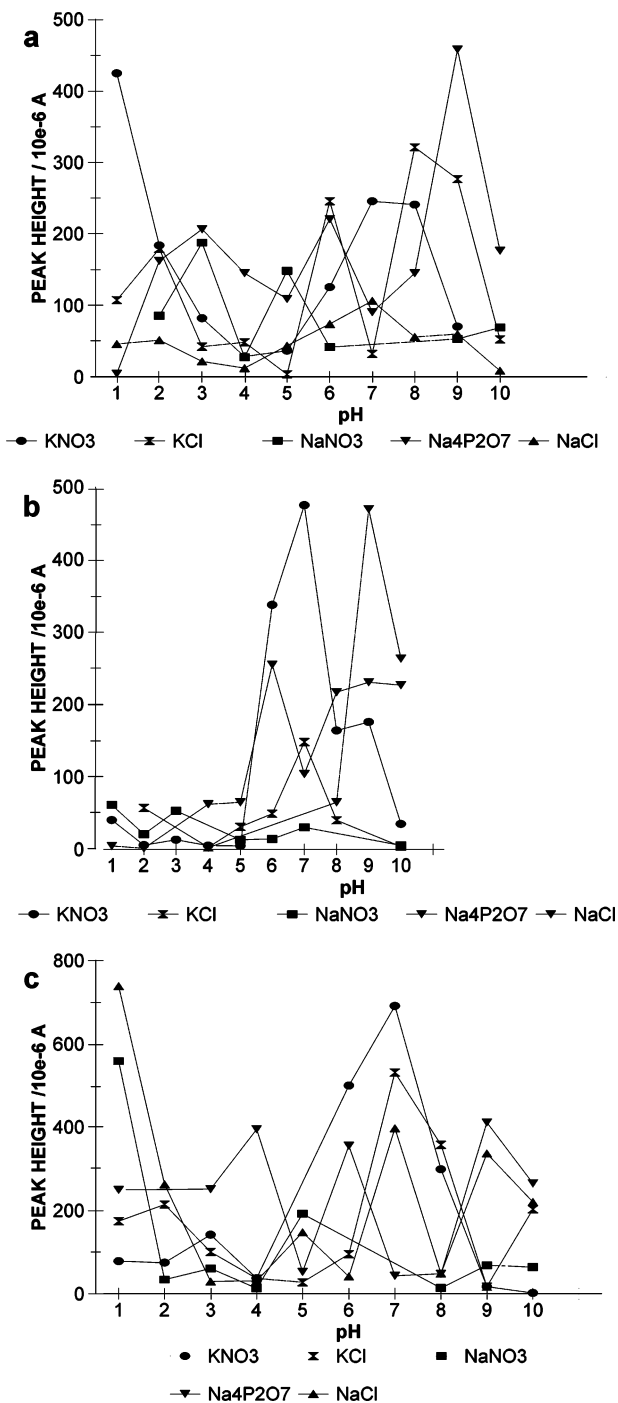


Figure 1. The effect of electrolyte and pH on the peak height for a concentration of Fe(II) solution of  $10^{-4}$  mol/L: (A) natural diamond, (B) synthetic-1, and (C) synthetic-2.

particle size ( $50\ \mu\text{m}$ ). Regarding the differences in the structures of natural and synthetic diamonds, the best behavior of the natural diamond-based electrode proved that because of uncontrolled development of the monocrystals, it presents more structural defects than the synthetic diamonds, which are made using a well-known controlled synthesis.

The responses of the electrodes to different Fe(II) concentrations were linear over wide concentration ranges (Figure 2) and can be described by the following equations of calibration (a, natural diamond; b, synthetic-1; and c, synthetic-2),

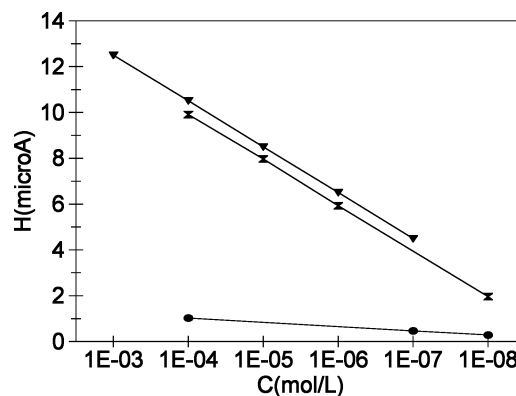


Figure 2. Calibration graphs of the electrodes based on (A) natural diamond, (B) synthetic-1, and (C) synthetic-2.

$$H = 0.37 + 6.11C, \quad r = 0.9707 \quad (\text{a})$$

$$H = 7.50 + 5.30C, \quad r = 0.9543 \quad (\text{b})$$

$$H = 1.84 + 969.15C, \quad r = 0.9983 \quad (\text{c})$$

where  $H$  is the peak height ( $\mu\text{A}$ ),  $C$  is the concentration of Fe(II) (mmol/L), and  $r$  is the regression coefficient.

The limits of detection were calculated accordingly with Otto,<sup>25</sup>

$$\text{DL} = \frac{I_B + 3\sigma_S - a}{S}$$

where  $I_B$  is the background current recorded,  $\sigma_S$  is the standard deviation for the measurement of the background current,  $a$  is the intercept of the calibration equation, and  $S$  is the slope of the calibration equation. The peak heights for natural diamond and synthetic diamond-2 were proportional to the Fe(II) concentration between  $10^{-8}$  and  $10^{-4}$  mol/L, with detection limits of  $10^{-10}$  and  $10^{-9}$  mol/L, respectively. For the synthetic diamond-1, the linear concentration range was between  $10^{-7}$  and  $10^{-3}$  mol/L, with a detection limit of  $10^{-8}$  mol/L.

The peak profiles obtained using DPV for the assay of two different concentrations of Fe(II) with the three electrodes are shown in Figure 3A–C, and the peak profiles obtained using DPV for the assay of  $10^{-5}$  mol/L Fe(II) with glassy carbon (GC) and carbon paste (CP) electrodes are shown in Figure 4A and B. At 75 mV, the background current was 340 nA, 7.47  $\mu\text{A}$ , and 1.78  $\mu\text{A}$  for the electrodes based on natural, synthetic-1, and synthetic-2 diamonds. Accordingly, the signal-to-background ratio for the diamond paste-based electrodes is very high. Furthermore, an analysis of the electrochemical noise was performed for all the diamond paste electrodes, and the results were compared with those obtained for GC and CP electrodes. This analysis proved that when the diamond was used as electrode material, the noise decreased 100 times for natural diamond and 10 times for both synthetic diamonds. If one also compares the height of the peaks obtained for the assay of a  $10^{-5}$  mol/L Fe(II) solution using natural diamond (1  $\mu\text{A}$ ), synthetic-1- (8.5  $\mu\text{A}$ ), and synthetic-2-based (8  $\mu\text{A}$ ) electrodes with those obtained using GC (0.244  $\mu\text{A}$ ) and CP (0.25  $\mu\text{A}$ ), one can easily see that the peak height increases greatly

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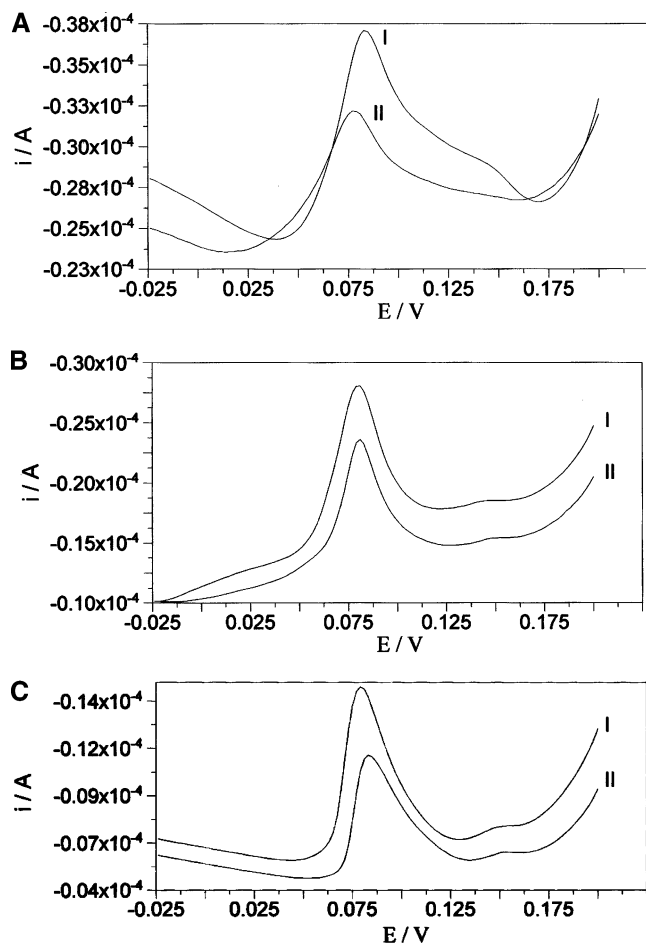


Figure 3. Peak profiles for DPV measurements when the electrodes based on (A) natural diamond (I,  $C_{\text{Fe(II)}} = 10^{-4}$  mol/L; II,  $C_{\text{Fe(II)}} = 10^{-6}$  mol/L), (B) synthetic-1 (I,  $C_{\text{Fe(II)}} = 10^{-3}$  mol/L; II,  $C_{\text{Fe(II)}} = 10^{-4}$  mol/L), and (C) synthetic-2 (I,  $C_{\text{Fe(II)}} = 10^{-5}$  mol/L; II,  $C_{\text{Fe(II)}} = 10^{-6}$  mol/L) are used.

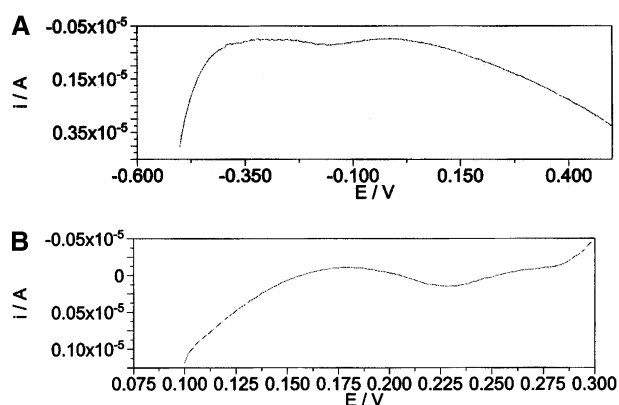


Figure 4. Peak profiles for DPV measurements when the electrodes based on (A) GC and (B) CP are used for the assay of Fe(II) ( $C_{\text{Fe(II)}} = 10^{-5}$  mol/L).

for the diamond paste-based electrodes. It follows that the signal/noise (S/N) ratio increases considerably when diamond paste electrodes are used for the assay of Fe(II) (e.g., for the assay of a  $10^{-5}$  mol/L Fe(II) solution using natural diamond-, synthetic-1-, and synthetic-2-based electrodes and GC and CP, the S/N ratio was  $1.11 \times 10^{14}:1$ ,  $1.14 \times 10^{14}:1$ ,  $1.65 \times 10^{14}:1$ ,  $1.74 \times 10^{12}:1$ , and  $1.47 \times 10^{12}:1$ , respectively).

Table 1. Amperometric Selectivity Coefficients<sup>a</sup>

interfering species (J)	electrode based on		
	natural diamond	synthetic-1	synthetic-2
	$K^{\text{amp}}$		
$\text{Mg}^{2+}$	$1.20 \times 10^{-3}$	$3.50 \times 10^{-3}$	$1.10 \times 10^{-3}$
$\text{Cr}^{3+}$	$2.10 \times 10^{-3}$	$3.26 \times 10^{-3}$	$1.25 \times 10^{-3}$
$\text{Mn}^{2+}$	$2.30 \times 10^{-3}$	$8.29 \times 10^{-3}$	$1.18 \times 10^{-3}$
$\text{Cu}^{2+}$	$6.67 \times 10^{-4}$	$4.78 \times 10^{-3}$	$8.14 \times 10^{-4}$
$\text{Zn}^{2+}$	$1.91 \times 10^{-3}$	$1.00 \times 10^{-3}$	$3.36 \times 10^{-3}$

<sup>a</sup> All measurements were made at 25 °C; all values are the average of ten determinations.

The reproducibility of peak current obtained using the diamond paste-based electrodes was good, as proved by the values of relative standard deviation (RSD < 1%).

**Selectivity of the Diamond Paste Electrodes.** The effect of various ions (that are found in the compositions of the vitamins from where Fe(II) was determined) on the peak height of Fe(II) was examined for all diamond paste electrodes. Furthermore, the effect of  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$ , and  $\text{K}^{+}$  on the peak height was determined. Mixed and separate solution methods were used in order to determine the amperometric selectivity coefficients.<sup>24</sup> The ratio between iron(II) and the possible interfering agent was 1:10 (mol/mol). The results obtained for the amperometric selectivity coefficients using the mixed solutions method (Table 1) indicate that all ions investigated,  $\text{Mg}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ , do not interfere with the determination of  $\text{Fe}^{2+}$ . For  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$ , and  $\text{K}^{+}$ , the amperometric selectivity coefficients were  $<10^{-5}$ . Accordingly, they do not interfere in the assay Fe(II).

**Analytical Application.** The response characteristics as well as the selectivity of the diamond paste electrodes made them suitable for the determination of Fe(II) in pharmaceutical products as well as in water and biological fluids. The recovery tests performed for Fe(II) solution using DPV were higher than 99.00% with RSD (%) values <1% ( $N = 10$ ). The results obtained for the uniformity content test of four different vitamin tablets using the diamond paste-based electrodes are shown in Table 2, and they are comparable with those obtained using a standard method<sup>26</sup> (sample 1, 12.90 mg Fe(II)/tablet; sample 2, 17.85 mg Fe(II)/tablet; sample 3, 7.20 mg Fe(II)/tablet; and sample 4, 2.90 mg Fe(II)/tablet). Fe(II) can be reliably assayed from the tablets with a high average recovery and low RSD% values. All of the values for the recovery (%) of Fe(II) fall within the labeled amount of 90–110% required by the USP XXV.<sup>26</sup> The advantage of the proposed method is the simplicity and also the high precision due to the lower values of the RSD (%).

**Statistical Comparison between the Results Obtained for the Uniformity Content Test of Vitamins Tablets Using the Diamond Paste-Based Electrodes.** Mathematical calculations and statistical treatment of analytical data were performed for all the vitamins samples using the paired *t*-test approach.<sup>27</sup> The idea was to examine whether the different diamond paste-based electrodes gave results that differed significantly at the 95%

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Table 2. Uniformity Content Test for Vitamins<sup>a</sup>

sample	mg Fe(II)/tablet	av recovery, Fe(II) mg/tablet
Electrode Based on Natural Diamond		
1	13.0	12.94 ± 0.12
2	18.0	17.82 ± 0.22
3	7.5	7.18 ± 0.08
4	5.0	4.87 ± 0.04
Electrode Based on Synthetic-1		
1	13.0	12.93 ± 0.14
2	18.0	17.83 ± 0.21
3	7.5	7.17 ± 0.08
4	5.0	4.86 ± 0.05
Electrode Based on Synthetic-2		
1	13.0	12.94 ± 0.13
2	18.0	17.84 ± 0.21
3	7.5	7.18 ± 0.08
4	5.0	4.86 ± 0.04

<sup>a</sup> All measurements were made at 25 °C; all values are the average of ten determinations.

confidence level ( $N = 10$ ).  $t_{\text{calculated}}$  ( $t_{\text{calc}}$ ) was computed using the following formula,<sup>26</sup>

$$t_{\text{calc}} = |\bar{X}_1 - \bar{X}_2| \sqrt{\frac{N(N-1)}{\sum (d_i - \bar{d})^2}}$$

where  $\bar{X}_1$  and  $\bar{X}_2$  are the average recoveries of Fe(II) for each sample,  $N$  is the number of measurements,  $\bar{d}$  is the mean of  $d_i$  values and  $d_i$  is the individual difference between the two methods for each sample. As can be seen from Table 3, all of the  $t_{\text{calc}}$  values at the 95% confidence level are less than the tabulated theoretical value, 2.262. It follows that there is no statistically significant difference between the results obtained for the uniformity content test of Fe(II) using the proposed diamond paste-based electrodes.

Table 3. Statistical Evaluation of the Uniformity Content Test Performed with the Proposed Diamond Paste-Based Electrodes

sample	electrode based on		
	natural diamond vs synthetic-1	synthetic-1 vs synthetic-2	natural diamond vs synthetic-2
1	1.04	$t_{\text{calc}}$ 1.13	
2	0.39	0.58	0.89
3	0.28	1.44	
4	1.55		1.92

## CONCLUSION

The new class of diamond electrodes, namely, diamond paste-based electrodes provides excellent features for the detection of Fe(II) in pharmaceutical products, biological fluids, food, and water. The design of the diamond paste-based electrode is simple, fast, and reproducible. The reliability of the analytical information is assured by the low RSD (<5%) values obtained in the recovery tests, by the fast response of the differential pulse voltammetry (DPV), and by its large working concentration range. The proposed new diamond paste electrode has high sensitivity and stability. By utilization of diamond paste-based electrodes, the noise is reduced considerably. The signal/noise ratio increased if one compares these new values with those obtained when a carbon paste or glassy carbon electrodes are used for the same measurements.

The diamond paste electrodes may be used for the assay of Fe(II) in water, wine, and biological fluids. Because of the high biocompatibility of the diamond material, after miniaturization, the diamond paste-based electrodes may be tested for in vivo analysis of Fe(II).

Received for review November 11, 2002. Accepted July 16, 2003.

AC026300B